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# Optimal temperature profiles for parallel-consecutive reactions with deactivating catalyst

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**Abstract**

A cocurrent tubular reactor with temperature profile control and recycle of moving deactivating catalyst has been investigated. For the temperature-dependent catalyst deactivation, the optimization problem has been formulated in which a maximum of a profit flux is achieved by the best choice of temperature profile and residence time of reactants for the set of catalytic reactions $A + B \rightarrow R$ and $R + B \rightarrow S$ with desired product R, the rates of reactions have been described separately for every reagent by the expressions containing (temperature dependent) reaction rate constants, concentrations of reagents, catalyst activity, as well as catalyst concentration in the reacting suspension and a measure of the slip between reagents and solid catalyst particles. The algorithms of maximum principle have been used for optimization. The optimal solutions show that a shape of the optimal temperature profile depends on the mutual relations between activation energies of reactions and catalyst deactivation. It has been proved that the optimal temperature profile is a result of the compromise between the overall production rate of desired reagent R (production rate in the first reaction minus disappearance rate in the second one), necessity of saving of reagents residence time (reactor volume) and necessity of saving catalyst; the most important influence on the optimal temperature profile is associated with necessity of saving the catalyst. When catalyst recycle ratio increases (mean number of catalyst particles residing in reactor increases), optimal temperatures save the catalyst, as the optimal profile is shifted in direction of lower temperatures. The same is observed when catalyst slip increases (catalyst residence time in reactor increases). Despite of variation in the catalyst concentration the optimal profile is practically the same because the decay rate is affected only by instantaneous activity of catalyst. When reactor unit volume price decreases, catalyst residence time increases, whereas optimal temperature profile is shifted to lower temperatures. When economic value of unit activity of outlet catalyst increases (catalyst with a residual activity still has an economic value), catalyst saving should be more and more intense. As far as possible, the optimal profile is shifted in direction of lower temperatures, whereas the optimal residence time is still the same. Then the optimal profile is isothermal at the level of minimum allowable temperature, whereas the catalyst is saved as its residence time in reactor decreases. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Cocurrent tubular reactor; Deactivating catalyst; Decay rate; Optimal temperature; Reactor volume

## 1. Introduction

An optimization problem, which regularly appears for various catalytic reactors is that of optimal temperature control. Examples of catalytic reactors where the problem is important were described in the article [1] constituting extended version of the symposium paper [2]. A frequently encountered reaction system involves a set of parallel-consecutive reactions (1) and (2), with a desired product R, which run in a tubular reactor with moving deactivating catalyst (granular solid).

$$A + B \overset{E_1, k_{10}}{\rightarrow} R \tag{1}$$

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**Nomenclature**

| | |
|---|---|
| $a$ | catalyst activity defined as the ratio of reaction rate in the presence of current catalyst and the rate in the presence of fresh catalyst (dimensionless) |
| $a_f$ | fresh catalyst activity |
| $A_s$ | fresh catalyst surface area per unit mass of catalyst ($m^2$/kg) |
| $c_i$ | concentration of reagent $i$ (mol/l) |
| $E_d$ | activation energy of catalyst deactivation (J/mol) |
| $E_i$ | activation energy of reaction $i$ (J/mol) |
| $F$ | process profit flux (Eq. (21)) ($) |
| $H$ | modified reactor unit volume price ($/s) |
| $k_d$ | catalyst deactivation rate constant ($min^{-1}$) |
| $k_i$ | reaction rate constant (1/(mol min)) |
| $k_{d0}$ | frequency factor in Arrhenius expression for $k_d$ ($min^{-1}$) |
| $k_{i0}$ | frequency factor in Arrhenius expression for $k_i$ (1/(mol min)) |
| $K_c$ | flux of fixed cost ($/min) |
| $L$ | reactants mass flux in reactor (kg/min) |
| $M_R$ | molar mass of desired reagent R (kg/mol) |
| $P$ | measure of the slip between reagents and catalyst (granular solid) (Eq. (13)) |
| $r_{fA}$ | reaction rate for reagent A in presence of fresh catalyst related to the unit volume of reactants mixture |
| $r_{sfA}$ | reaction rate for reagent A in presence of fresh catalyst related to the unit area of catalyst |
| $R$ | gas constant or catalyst recycle ratio (Eq. (3)) (kg/kg) |
| $S$ | catalyst mass flux in reactor (kg/min) |
| $S_f$ | fresh catalyst mass flux (kg/min) |
| $S_r$ | recycled catalyst mass flux (kg/min) |
| $t$ | time (min) |
| $t_k$ | residence time of reactants in reactor (min) |
| $t_{sk}$ | residence time of catalyst (solid particles) in reactor (min) |
| $T$ | temperature (K) |
| $T_*$,$T^*$ | minimum and maximum allowable temperature, respectively (K) |
| $u_L$ | velocity of reacting mixture in the reactor (m/s) |
| $u_s$ | velocity of catalyst in the reactor (m/s) |
| $V_L$ | volume of reactants mixture ($m^3$) |
| $V_r$ | volume of reacting suspension ($m^3$) |
| $V_s$ | volume of solid catalyst ($m^3$) |
| $Y$ | parameter defined by Eq. (16) |

*Greek symbols*

| | |
|---|---|
| $\varepsilon$ | voidage of reacting suspension |
| $\kappa$ | economic value of unit activity of outlet catalyst ($/kg) |
| $\mu_f$ | unit price of fresh catalyst ($/kg) |
| $\mu_R$ | unit price of desired reagent R ($/kg) |
| $\rho_L$ | density of reactants mixture ($kg/m^3$) |
| $\rho_s$ | density of catalyst ($kg/m^3$) |

$$R + B \xrightarrow{E_2,\, k_{20}} S \tag{2}$$

The cocurrent tubular reactor with catalyst recycle, Fig. 1, is analysed. We designate — $L$: reactants mass flux; $c[0]$ and $c[t_k]$: inlet and outlet concentrations of reactants; $t_k$: residence time of reactants; $a_f$, $a[0]$ and $a[t_k]$: fresh, inlet and outlet catalyst activity, respectively.

Catalyst mass flux in reactor $S$ is a sum of fluxes of fresh $S_f$ and recycled $S_r$ catalyst, $S = S_r + S_f =$ constant, whereas catalyst recycle ratio $R$ is defined as:

$$R = \frac{S_r}{S_f} \tag{3}$$

For a temperature-dependent and concentration-independent catalyst deactivation, deactivation rate can be described [3] by Eq. (4) where $t_{sk}$ is the residence time of catalyst (solid particles). Catalyst activity $a$ is defined as the ratio of reaction rate in the presence of given catalyst and reaction rate in the presence of fresh catalyst.

$$\frac{da}{dt_s} = -k_d a = -k_{d0} \exp\left(\frac{-E_d}{RT}\right) a \tag{4}$$

Our purpose here is the formulation and solution of the optimization problem in which a maximum of a process profit flux is achieved by the best choice of

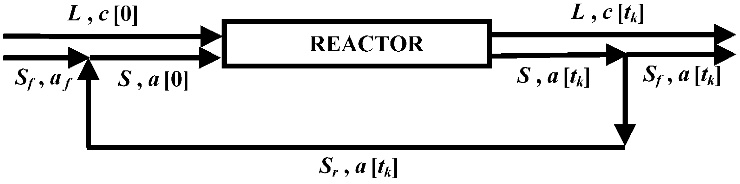

Fig. 1. Cocurrent tubular reactor with catalyst recycle.

temperature profile along reactor as well as the best choice of residence time of reactants in the reactor.

## 2. Formulation of optimization problem

The rates of catalytic reactions (1) and (2) can be described by a set of four equations, separately for every reagent $i$ = A, B, R, S. Considering, for example, the reaction rate for reagent A and referring this rate to the unit area of fresh catalyst, it can be written as

$$r_{\mathrm{sfA}} = k_1[T]c_{\mathrm{A}}c_{\mathrm{B}} \tag{5}$$

where $k_1[T]$ satisfies the Arrhenius equation. Index s is related to the surface of solid catalyst, f to fresh catalyst and A to reagent A. The reaction rate for reagent A in the presence of fresh catalyst can also be related to the unit volume of reactants mixture, $r_{\mathrm{fA}}$, hence

$$r_{\mathrm{fA}}\,\mathrm{d}V_{\mathrm{L}} = r_{\mathrm{sfA}}\,\mathrm{d}A_{\mathrm{f}} \tag{6}$$

where $\mathrm{d}V_{\mathrm{L}}$ is the elementary volume of reactants mixture and $\mathrm{d}A_{\mathrm{f}}$ the elementary surface area of fresh catalyst satisfying following relationship

$$\mathrm{d}A_{\mathrm{f}} = A_{\mathrm{s}}\rho_{\mathrm{s}}\,\mathrm{d}V_{\mathrm{s}} \tag{7}$$

where $A_{\mathrm{s}}$ is the fresh catalyst surface area per unit mass of catalyst, $\rho_{\mathrm{s}}$ the catalyst density and $\mathrm{d}V_{\mathrm{s}}$ the elementary volume of solid catalyst. As the elementary volume of reacting suspension $\mathrm{d}V_{\mathrm{r}}$ satisfies following equation:

$$\mathrm{d}V_{\mathrm{r}} = \mathrm{d}V_{\mathrm{L}} + \mathrm{d}V_{\mathrm{s}} \tag{8}$$

voidage of reacting suspension can be written as

$$\varepsilon = \frac{\mathrm{d}V_{\mathrm{L}}}{\mathrm{d}V_{\mathrm{r}}} = \frac{\mathrm{d}V_{\mathrm{L}}}{\mathrm{d}V_{\mathrm{L}} + \mathrm{d}V_{\mathrm{s}}} \tag{9}$$

Applying Eqs. (7)–(9) in Eq. (6) one can obtain Eq. (10) which describes $r_{\mathrm{fA}}$, which is the reaction rate for reagent A in the presence of fresh catalyst related to the unit volume of reactants mixture.

$$r_{\mathrm{fA}} = \frac{1-\varepsilon}{\varepsilon}A_{\mathrm{s}}\rho_{\mathrm{s}}r_{\mathrm{sfA}} \tag{10}$$

This result is compatible with an expression obtained by Aris [4] for non-deactivating catalyst. For deactivating catalyst Eq. (10) takes the following form

$$r_{\mathrm{fA}} = \frac{1-\varepsilon}{\varepsilon}aA_{\mathrm{s}}\rho_{\mathrm{s}}r_{\mathrm{sfA}} \tag{11}$$

where $a = a[t]$ which is a function of time.

We can now introduce the dimensionless catalyst flux in reactor $\beta$ defined as

$$\beta = \frac{S/\rho_{\mathrm{s}}}{L/\rho_{\mathrm{L}}} \tag{12}$$

where $L$ is the reactants mass flux, $S$ the catalyst mass flux and $\rho_{\mathrm{s}}$ and $\rho_{\mathrm{L}}$ are the densities of catalyst and reactants mixture, respectively. Moreover we introduce the parameter $P$ constituting the measure of the slip between reagents and catalyst (granular solid), defined as

$$P = \frac{u_{\mathrm{L}}}{u_{\mathrm{s}}} \tag{13}$$

where $u_{\mathrm{L}}$ and $u_{\mathrm{s}}$ describe, respectively, the velocities of reacting mixture and catalyst in the reactor. It is then easy to show that following relationship is valid:

$$\varepsilon = \frac{1}{1+P\beta} \tag{14}$$

and, therefore, Eq. (11) takes the following form:

$$r_{\mathrm{fA}} = Y[\beta]\,ar_{\mathrm{sfA}} \tag{15}$$

where

$$Y[\beta] = PA_{\mathrm{s}}\rho_{\mathrm{s}}\beta \tag{16}$$

After applying of Eq. (5), relationship (15) can be written in the following form:

$$-\frac{\mathrm{d}c_{\mathrm{A}}[t]}{\mathrm{d}t} = r_{\mathrm{fA}} = Y[\beta]k_1[T]a[t]c_{\mathrm{A}}[t]c_{\mathrm{B}}[t] \qquad (17)$$

where the temperature control $T$ is a function of time $t$. In optimization we search for an optimal temperature profile $T[t]$.

The rates of catalytic reactions for reagents B, R and S can be written in the form of equations of the same type as Eq. (17). Of course, stoichiometry of Eqs. (1) and (2) has to be taken into account.

With Eq. (13) taken in the form

$$P = \frac{u_{\mathrm{L}}}{u_{\mathrm{s}}} = \frac{t_{\mathrm{sk}}}{t_{\mathrm{k}}} = \frac{t_{\mathrm{s}}}{t} \qquad (18)$$

Eq. (4) describing catalyst deactivation rate can be written as

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -Pk_{\mathrm{d}}a = -Pk_{\mathrm{d0}}\exp\left(\frac{-E_{\mathrm{d}}}{RT[t]}\right)a \qquad (19)$$

Eqs. (17), (19) and similar equations for all independent components constitute the set of state equations in the sense understood in optimization. These equations are optimized subject to given initial conditions $c_i$ and the following boundary condition for the catalyst activity:

$$a[0] = \frac{S_{\mathrm{f}}a_{\mathrm{f}} + S_{\mathrm{r}}a[t_{\mathrm{k}}]}{S_{\mathrm{f}} + S_{\mathrm{r}}} = \frac{a_{\mathrm{f}} + Ra[t_{\mathrm{k}}]}{1+R} = \frac{1 + Ra[t_{\mathrm{k}}]}{1+R} \qquad (20)$$

The maximization problem for optimization of the process profit flux is considered. The process profit flux, $F$, is defined as the difference between the sum of outlet value fluxes and the sum of inlet value fluxes

$$F = \frac{L}{\rho_{\mathrm{L}}}c_{\mathrm{R}}[t_{\mathrm{k}}]M_{\mathrm{R}}\mu_{\mathrm{R}} + S_{\mathrm{f}}\kappa a[t_{\mathrm{k}}] - S_{\mathrm{f}}\mu_{\mathrm{f}} - Ht_{\mathrm{k}} - K_{\mathrm{c}} \qquad (21)$$

The first term on the right-hand side of Eq. (21) describes flux value of desired reagent R, the second term — flux of value of outlet catalyst (catalyst with a residual activity still has an economic value), the third term — flux of fresh catalyst cost, the fourth term — flux of investment cost of reactor dependent on reactor volume expressed in terms of reagents residence time $t_{\mathrm{k}}$ and the last term — flux of fixed cost $K_{\mathrm{c}}$. The symbols mean — $M_{\mathrm{R}}$: molar mass of desired reagent R; $\mu_{\mathrm{R}}$: unit price of reagent R (\$/kg); $\kappa$: economic value of unit activity of outlet catalyst (\$/kg); $\mu_{\mathrm{f}}$: unit price of fresh catalyst (\$/kg); $H$: modified reactor unit volume price (\$/s); $K_{\mathrm{c}}$: fixed cost (\$).

The process profit flux $F$ has to be maximized whereas the optimal temperatures have to reside in an allowable range defined as

$$T_* \le T[t] \le T^* \qquad (22)$$

where $T_*$ and $T^*$ describe minimum and maximum allowable temperatures, respectively.

## 3. Shapes of the optimal temperature profiles

With the help of standard algorithm of continuous optimization, the Pontryagin's maximum principle [5], the optimal temperature profiles which maximize the profit flux are obtained. The shapes of these optimal profiles for various relations between activation energies of reations $E_1$ and $E_2$, as well as activation energy of catalyst deactivation $E_{\mathrm{d}}$ are presented in Fig. 2 (versus time $t$ or relative length $l/l_{\mathrm{k}}$).

If activation energy of reaction (1), $E_1$, is greater than activation energy of reaction (2), $E_2$, and greater than activation energy of catalyst deactivation, $E_{\mathrm{d}}$, the optimal temperature profile is always an isothermal one located on the level of maximum allowable temperature $T^*$. This is shown by the upper sketch in Fig. 2.

If $E_1 < E_2, E_{\mathrm{d}}$ or $E_{\mathrm{d}} < E_1 < E_2$ the optimal temperature profile, in general case, has its minimum — the middle sketch in Fig. 2. In particular case the optimal temperature profile can be represented by some cutting of general profile; for $E_{\mathrm{d}} < E_1 < E_2$ the optimal temperature profile has to start always with the maximum allowable temperature $T^*$.

If $E_2 < E_1 < E_{\mathrm{d}}$ the optimal temperature profile, in general case, has its maximum — the lower sketch in Fig. 2. In particular case the optimal temperature profile can be represented by some cutting of general profile; if outlet catalyst is worthless, $\kappa = 0$, optimal temperature profile has to be always ended by $T^*$.

Burghardt and Skrzypek [6] have presented shapes of the optimal temperature profiles for the set of reactions (1) and (2) undergoing, however, in the presence

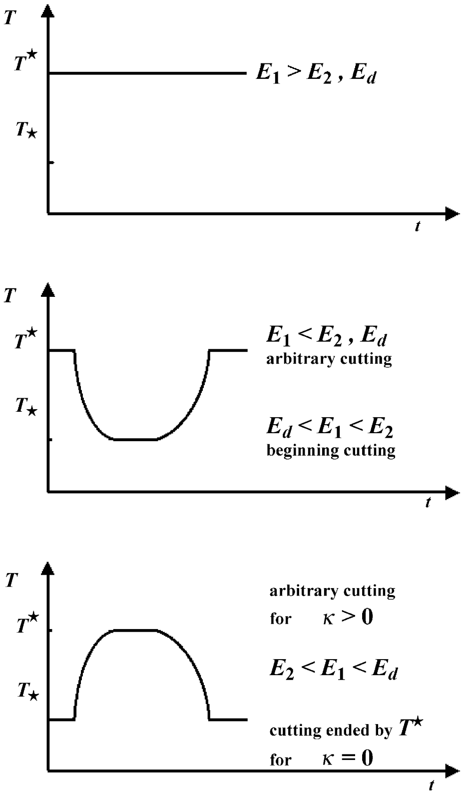

Fig. 2. Shapes of the optimal temperature profiles for various relations between activation energies of reactions $E_1$ and $E_2$, as well activation energy of catalyst deactivation $E_\mathrm{d}$.

of non-deactivating catalyst then activation energy for the catalyst deactivation process $E_\mathrm{d}$ is absent there. For $E_1 > E_2$ they obtained the shape of the optimal temperature profile like the one presented in the upper sketch of Fig. 2, whereas for $E_1 < E_2$ — like the one presented in the middle sketch of Fig. 2, the process always start with the maximum allowable temperature $T^*$. Our middle sketch in Fig. 2 generalizes the results [6] which refer only to the case with $E_1 < E_2 < E_\mathrm{d}$ and when $E_\mathrm{d}$ approaches to infinity.

## 4. Results of numerical computations

The results were obtained for the following data [1,2]: $c_\mathrm{A}[0] = c_\mathrm{B}[0] = 1\,\mathrm{mol/l}$, $c_\mathrm{R}[0] = c_\mathrm{S}[0] = 0$, $E_1 = 67\,\mathrm{kJ/mol}$, $E_2 = 125\,\mathrm{kJ/mol}$, $E_\mathrm{d} = 105\,\mathrm{kJ/mol}$, $k_{10} = 5 \times 10^3\,\mathrm{l^2/(mol\,min\,m^2)}$, $k_{20} = 3 \times 10^{10}\,\mathrm{l^2/(mol\,min\,m^2)}$, $k_{\mathrm{d}0} = 4 \times 10^{15}\,\mathrm{min^{-1}}$, $T_* = 335\,\mathrm{K}$ and $T^* = 355\,\mathrm{K}$. The discrete optimization algorithm [7] was applied in computations.

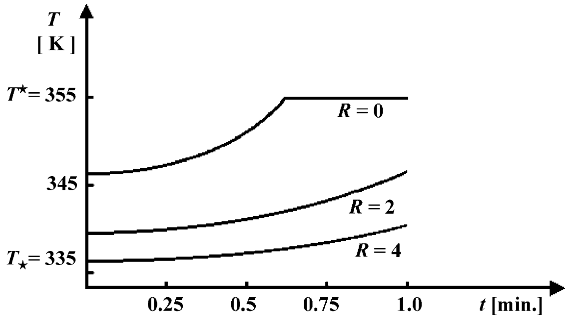

Fig. 3. Optimal temperature profiles for various values of catalyst recycle ratio $R$.

The results and their analysis expose shapes of optimal temperature profiles as the effect of compromise between the overall production rate of desired reagent R (production rate in the first reaction minus disappearance rate in the second one), necessity of saving of reagents residence time (reactor volume) and necessity of saving catalyst.

The results presented below show that in the optimal reactor (with reactions subject to the temperature-dependent catalyst deactivation) the most important influence on the optimal temperature profile is associated with necessity of saving the catalyst:

- When catalyst recycle ratio $R$ increases (mean number of catalyst particles residing in reactor increases) the optimal temperatures save catalyst as the optimal profile is shifted in direction of lower temperatures (Fig. 3). The same is observed when catalyst slip $P$ increases (particle residence time in reactor increases) (Fig. 4). In this context we

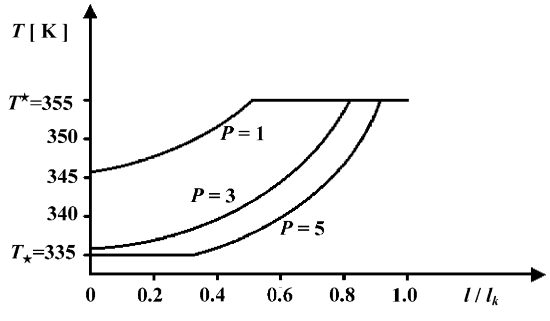

Fig. 4. Optimal temperature profiles for various values of catalyst slip $P$.

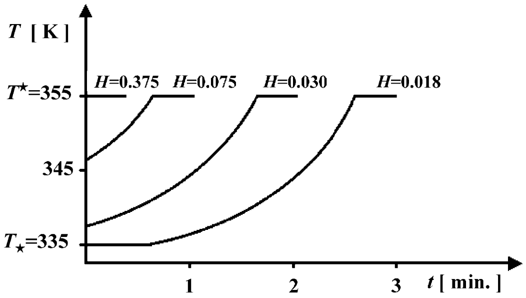

Fig. 5. Optimal temperature profiles for various values of reactor unit volume price $H$.

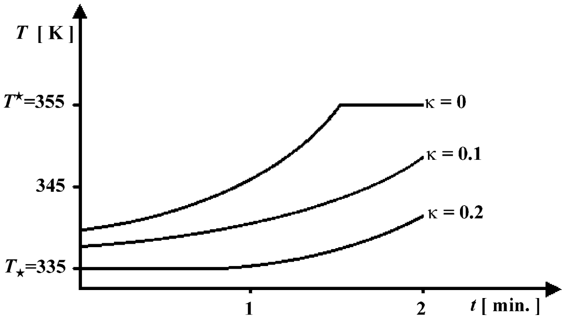

Fig. 6. Optimal profiles for various economic values of unit activity of outlet catalyst $\kappa$.

point out an essential role of the catalyst slip in the mathematical model, an evergreen problem which is not treated sufficiently clearly to date.

- Despite of variation in catalyst concentration $\beta$ the optimal profile is practically the same because the decay rate is affected only by instantaneous activity of catalyst.
- When unit volume price of reactor, $H$, decreases, catalyst residence time increases, and optimal temperatures save catalyst; the optimal profile is shifted in direction of lower temperatures (Fig. 5).
- When economic value $\kappa$ of unit activity of outlet catalyst increases (catalyst with a non-vanishing activity still has an economic value), catalyst saving should be more and more intense. As far as possible, the optimal profile is shifted in the direction of lower temperatures whereas the optimal residence time is still the same. The optimal profile is then isothermal, at the level of minimum allowable temperature $T_*$, whereas catalyst is saved as the catalyst residence time in reactor decreases (same as the reagents residence time) (Figs. 6 and 7).

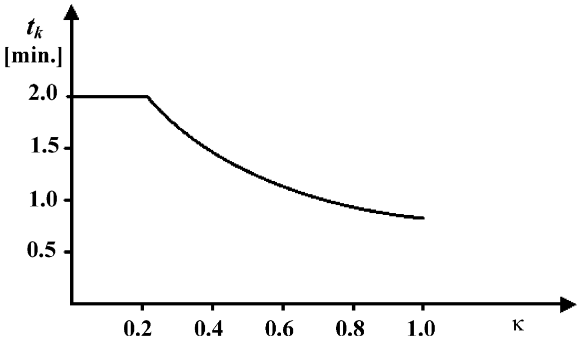

Fig. 7. Optimal residence time for various economic values of unit activity of outlet catalyst $\kappa$.

Our results show that even partial or approximate implementation of various forms of catalyst saving predicted by optimization can result in a remarkable reduction of costs.

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